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**(54) A METHOD OF WORKING-UP WASTE SLAG FROM OXYGEN STEEL PRODUCTION**

(71) We, EERSTE NEDERLANDSE CEMENT INDUSTRIE (ENCI) N.V., a Dutch company, of Lage Kanaaldijk 115, Maastricht, the Netherlands, and C.B.R. Cementbedrijven N.V., a Belgian company, of Terhulpssteenweg 185, B 1170 Brussels, Belgium, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described, in and by the following statement:-

The invention relates to a method for working-up waste slag from the oxygen steel production (hereafter to be called L.D.-slag), said method comprising reducing metal oxides being present in the slag to metal by means of a reducing agent and with the addition of an Al₂O₃-containing additive and separating them from the slag.

In certain areas often large amounts of slag are found, originating i.a. from the method of the oxygen steel production, the so-called "L.D.-slag". This slag, contrary to blast furnace slag, after cooling (quenching) is not hydraulic and so not very valuable. The possibility of recycling the slag in a blast furnace to extract the iron is limited as a result of accumulation of undesired elements. The waste piles of this slag can so be considered as being detrimental to the environment.

The main components of the L.D.-slag are usually within the following limits:

20	SiO ₂	7 - 18% by weight	20
	Al ₂ O ₃	0.3 - 2% by weight	
	CaO	35 - 55% by weight	
25	MgO	2.6 - 6% by weight	25
	Fe + FeO _x	15 - 40% by weight	
	MnO _x	2 - 6.5% by weight	
30	P ₂ O ₅	1 - 2.5% by weight	30

The iron content of the slag is such that extraction of iron from the slag appears useful. Extraction of the iron from the slag by a simple reduction treatment is difficult and economically little remunerative. In a reducing atmosphere at a temperature of about 1200°C, it is true, metallic iron is formed, but this iron remains finely divided in the pores of the remaining slag because the temperature at which this slag becomes liquid is considerably increased by reducing the iron compounds. The iron can hardly be separated from the remaining slag.

French patent application 73 05145 shows a method of extracting metal from a L.D.-slag, with which method also a slag that can still be used for certain applications is obtained. One starts from a liquid L.D.-slag, to which bauxite is added. Starting from a liquid L.D.-slag the reduction still takes place at about 1600°C by means of a solid reducing agent such as carbon or aluminium. In areas where bauxite is a relatively expensive raw material, said method is not very attractive. One of the examples, however, indicates that besides

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Al_{23} also SiO_2 can be added to the flux, a slag being obtained that after cooling and grinding has hydraulic properties. Energetically this method is not attractive, especially if one would start from an already cooled slag (dumped material).

British patent specification 922 586 shows the extraction of iron from a slag, but this method is no more than a modified blast furnace process by the use of coke, iron ore and lime and cannot be used for the L.D.-slag. The remaining slag still contains rather much iron.

What is desired is a method for making-up L.D.-slag, said method allowing

- a) extraction of metal from the slag by reducing at relatively low temperature and not necessarily in the liquid phase, whereby advantageously an already cooled L.D.-slag (dumped material) can be used as starting material;
- b) the use as a flux additive of a material having a lower Al_2O_3 -content than bauxite, preferably a waste material;
- c) the separation of slag and metal at a relatively low temperature and preferably in a technologically simply way; while
- d) the remaining slag is an industrially useful product which preferably can be simply converted into a normal portland- or blast furnace cement.

The present invention provides a method of working up waste slag from oxygen steel production, L.D.-slag, comprising mixing solid L.D.-slag with an additive or additives containing an aluminium silicate, in a ratio of 55-97½ parts by weight of slag to 45-2½ parts by weight of the aluminium silicate, and with carbon as a reducing agent, the carbon being separate from and/or contained in the additive(s), heating the resulting mixture to between 1250°C and 1500°C so that metal oxides present in the slag are reduced to metal, and recovering iron from the newly formed slag.

After adding lime the newly formed slag can be converted into a portland cement clinker. By lime, materials are meant being high in CaO or CaCO_3 content. The complete L.D.-slag can be converted into valuable products according to the above method.

An important aspect of the invention is that simultaneously also other materials being detrimental to the environment can be used as additives and thus can be converted into a suitable product. This applies especially to the waste products of coal mines often to be found in the neighbourhood of steel industry, such as mine stones or stone sludge. Such waste products also often contain 15 to 24% by weight of carbon, which can simultaneously be used as a cheap reducing agent so that no or only a small amount of other reducing agents being rich in energy is necessary. This waste material can e.g. (not limitatively) have the following composition:

40	SiO_2	56% by weight	40
	Al_2O_3	25% by weight	
45	CaO	3% by weight	45
	Fe_2O_3	8% by weight.	

Besides these waste products from coal mines also fly ash being detrimental to the environment can be used. The chemical composition hereof corresponds with the one of schist ash. Also fly ash, schist, stone sludge, clays or clay-containing waste materials and the like can be used separately or mixed with each other.

In French patent application 73 05145 it is not disclosed that it is possible to use also aluminium silicates instead of bauxite, such as the mentioned waste materials of coal mines.

The ratio of L.D.-slag to added aluminium silicate can be varied within broad limits, dependent on the nature of the added aluminium silicate and the nature of the remaining new slag that is desired.

If one starts from waste stone of coal mines in a ratio, somewhat dependent on the composition of said stone, of 55-80 parts of L.D.-slag and 45 - 20 parts of schist (calculated on ash), then after separation of metal at 1350 to 1450°C a liquid slag is obtained, the composition of which is approximately the same as the one of a normal blast furnace slag. This slag after quenching can be processed into a hydraulic binding agent or as such be converted into portland cement clinker in a known way of applying lime.

Separating iron on the liquid phase has a number of disadvantages. Especially a rotary kiln cannot simply be used for said purpose.

According to the present invention it is possible to avoid these disadvantages if according

to a preferred method to the L.D.-slag so much additive is added that in the slag calcium silicate is present having the composition 2 CaO.SiO₂. This material has the property to disintegrate into a fine powder under the right cooling conditions and when present in the slag in a sufficient amount in the slag also can disintegrate said slag into a fine powder.

5 So more specifically to the L.D.-slag so much additive is added that the resulting slag in a triangular diagram representing the weight percentages of CaO, Al₂O₃ and SiO₂ is within an area of which, for a temperature of 1350°C, three vertices can be indicated having the following compositions:

		% CaO	% Al ₂ O ₃	% SiO ₂	
10		1.	55	3	42
15		2.	60	28	12
		3.	70	4	26

Every composition of the slag within the area comprised by these three vertices appears to lead to the spontaneous disintegration of the formed slag into a fine powder during 20 cooling to about 200°C.

It was also found that the metallic iron is present in the formed slag in finely divided state. After cooling and disintegration of the slag the iron particles then being present in ty powder can easily in a known way be separated from the powder, e.g. by magnetic forces, by air spearator and the like.

25 Surprisingly it also appeared that the size of the iron particles can be influenced. If additives are added such that the composition of the slag is close to the line connecting the points 1 to 2, the iron particles are considerably larger than the slag partcles, with a composition close to the point 3, however, their size does not differ much from the size of the slag particles. Therefore, for a good separation of iron and powdery slag the 30 composition will as much as possible be adjusted in the first mentioned area.

Said composition can be obtained by adding as an additive 20 - 2½ parts by weight of aluminium silicate, e.g. svist, with respect to 80 - 97½ parts by weight of L.D.-slag. In order 35 to reach the same result also many other additis can be added, together with the aluminium silicate. These other additives comprise aluminium oxide and silica containing materials: blast furnace slag, red muds and the like.

The formed powder after separating the iron can be converted into portland cement clinker in a known way by means of lime. A great advantage herewith is that the slag already available as a fine powder and that lime in decarbonated form is present in the slag.

40 A practical embodiment of the above mentioned preferred method consists in that L.D.-slag, additive and carbon are granulated, the granules are dried in a rotary kiln, are reduced and sctered, the granules are subsequently cooled to about 200°C while recovering the heat, whereafter the iron is separated from the disintegrated slag. This method with granules has the great advantage that in a simple way a rotary kiln can be used. The iron is initially included in the granules and hardly reoxidises.

45 The invention is illustrated by means of examples.

Example 1

In a laboratory mill (disc vibrating mill) 80 grammes of L.D.-slag, chemical analysis (all in percentages by weight): CaO-36.2%, SiO₂-13.5%, Al₂O₃-1.9%, MgO-4.4%, Fe₂O₃-34.1%, Mn-4.4% and P₂O₅-5%, were ground during 2 minutes together with 40 grammes 50 of schist waste from a coal washery. The chemical analysis of the schist was: CaO-1.2%, SiO₂-36.9%, Al₂O₃-17.1%, MgO-1.5%, Fe₂O₃-5.0%, P₂O₅-0.2%, loss on ignition - 32%.

The thus prepared raw materials were introduced into a crucible of sintered aluminium oxide and electrically heated in a resistance furnace up to a furnace temperature of 1400°C. 55 A reducing furnace atmosphere was maintained by placing the above mentioned crucible in a larger one, the bottom of which being covered with carbon. After a period of 30 minutes at 1400°C the crucible was removed from the furnace and cooled in the air to room temperature. Hereafter the content of the crucible was examined.

On the bottom of the crucible iron had been collected. The weight hereof was 21.7 60 grammes and the chemical analysis: Fe-94%, P-1.4%, Mn-0.9%, C-2.4%, Si-0.0%. Over the iron there were 76 grammes of slag, the chemical analysis of which was: CaO-38.2%, SiO₂-33.2%, Al₂O₃-12.4%, MgO-5.4%, Fe₂O₃-1.2%, MnO-3.9% and P₂O₅-0.2%.

In a laboratory mill 50 grammes of the obtained slag were ground during 2 minutes together with 105 grammes of limestone with chemical analysis: CaO-50.6%, SiO₂-6.2%, 65 Al₂O₃-0.9%, Fe₂O₃-0.4%, MgO-0.8% and an ignition loss of 40.9%. The obtained powder

was pressed into a tablet, whereafter the tablet was introduced into a platinum crucible and electrically heated in an resistance furnace to a furnace temperature of 1450°C. After heating for 30 minutes at 1450°C in an oxidizing atmosphere the crucible was removed from the furnace and cooled in the air.

5 The sintered tablet was microscopically examined; the material appeared not to deviate mineralogically from normal portland cement clinker.

Example 2

A L.D.-slag with chemical analysis (all percentages by weight):

10 CaO-39.2%, SiO₂-12.9%, Al₂O₃-1.9%, MgO-5.2%, Fe₂O₃-33.8%, MnO-4.9% and P₂O₅-1.7% and schist with chemical analysis:

CaO-0.4%, SiO₂-39.8%, Al₂O₃-15.2%, MgO-1.4%, Fe₂O₃-4.8%, ignition loss - 34.2% and pure carbon, were used for preparing mixtures A and B.

Mixture A consisted of 100 grammes of L.D.-slag, 15.1 grammes of schist and 4.5 grammes of carbon.

15 Mixture B consisted of 100 grammes of L.D.-slag, 20.4 grammes of schist and 3.3 grammes of carbon.

The mixtures A and B were separately ground in a laboratory mill (disc vibrating mill) during 2 minutes and thereafter granulated with water to granules of about 2 cm. The obtained granules of the mixtures A and B were separately introduced into a crucible of sintered aluminium oxide, lined at the inner side with a thin layer of silicon carbide and electrically heated in a resistance furnace up to a temperature of 1400°C. A reducing atmosphere was maintained in the crucible by covering said crucible with a refractory plate.

20 After a period of 60 minutes at 1400°C the heating was switched off and the furnace allowed to slowly cool down to 800°C, whereafter the crucible was removed from the and further cooled in the air.

25 The granules of sample A spontaneously disintegrated at a temperature of 230°C while the granules of sample B disintegrated at 180°C. In both cases the iron was present in the disintegrated material as agglomerated granules.

30 The measured particle size distribution of the iron and the remaining disintegrated slag are shown, in weight percentages in the following table.

Table

Sample	A		B	
Fractions	Slag	Iron	Slag	Iron
0.20 µm	50.5%	15.0%	61.1%	5.9%
20-40 µm	35.4%	30.6%	32.1%	15.7%
40-63 µm	1.7%	28.2%	0%	24.6%
63-150 µm	12.0%	18.4%	4.1%	23.7%
> 150 µm	0.4%	7%	2.7%	30.1%
Totally	100 %	100 %	100 %	100 %

35 From the table it appears that the granule distribution of the iron in sample B is coarser than in sample A. This is in agreement with the fact that the composition of the slag of sample B is closer to the line connecting the points 1 to 2 in the said triangular diagram.

40 The invention is further illustrated by means of a drawing. Figure 1 is a flow-sheet of a possible treatment of a L.D.-slag with additives for preparing iron and portland cement clinker by means of rotary kilns, in accordance with example 1. It is explicitly stated that the application of the present invention on a technical scale is not limited to the embodiment according to the example. Other technical embodiments are possible, e.g. with other furnaces than rotary kilns.

45 In the flow-sheet of Figure 1 at 11 L.D.-slag and at 12 schist (e.g. the waste stone of a coal mine) are supplied to a crusher 13 crushing the raw materials. At 14 the broken product is supplied to a rotary kiln 15 wherein the iron compounds of the L.D.-slag are reduced by the carbon being present with the schist, optionally supplemented with an other reducing agent. Ah16 heating gas is supplied to bring the mass in the furnace to the desired temperature. In the furnace the mass finally melts at about 1400°C and at 17 from the melt separated pig iron can be drained off. By means of a drain 18 finally the remaining new slag is extracted.

less good disintegrated slag. In the separator 34 the iron product 35 and remaining slag 36 are recovered. The slags 32 and 36 from which the iron is extracted can in a known way by means of chalk be calcined to portland cement clinker.

Summarizing the essence of the invention has to be appreciated in that the L.D.-slag, a material being detrimental to the environment with an other material, respectively materials being detrimental to the environment at relatively low temperature can be converted into pig iron and a material that can be used as a hydraulic product, or a material that can be processed according to usual methods thus forming a hydraulic product. However, the invention is not strictly limited to the use of an additive being a waste material. An other essence of the invention is that it is possible according to a preferred embodiment to use a rotary kiln without complications and to separate the formed iron in a very simple way while the slag becomes available in powder form for further processing into a portland cement clinker. Finally the method is energetically favourable.

WHAT WE CLAIM IS:-

15. 1. A method of working up waste slag from oxygen steel production, L.D.-slag, comprising mixing solid L.D.-slag with an additive or additives containing an aluminium silicate, in a ratio of 55-97½ parts by weight of slag to 45-2½ parts by weight of the aluminium silicate, and with carbon as a reducing agent, the carbon being separate from and/or contained in the additive(s), heating the resulting mixture to between 1250°C and 1500°C so that metal oxides present in the slag are reduced to metal, and recovering iron from the newly formed slag.
20. 2. A method as claimed in claim 1, in which 55-80 parts by weight of L.D.-slag are treated with 45-20 parts by weight of schist, circulated as ash, and iron is separated between 1350 and 1450°C.
25. 3. A method as claimed in claim 1, in which the additive comprises at least one of the following: waste products of coal mines, fly ash, schist, stone sludge, clay, and clay-containing waste products.
30. 4. A method as claimed in claim 1, in which the mixture composition, expressed in terms of CaO, Al₂O₃ and SiO₂ is within an area defined by the following three weight percentage points on a triangular phase diagram plotted for a temperature of 1350°C:

	% CaO	% Al ₂ O ₃	% SiO ₂	
1.	55	3	42	
2.	60	28	12	35
3.	70	4	26	

40. the said composition is granulated, the resulting granules are dried and heated to at most 1400°C, the granules are then cooled to a temperature at which the granules disintegrate, and the iron is separated from the disintegrated granules.

45. 5. A method as claimed in claim 4, in which the composition substantially lies on a straight line connecting the following points 1 and 2:

	% CaO	% Al ₂ O ₃	% SiO ₂	
1.	55	3	42	
2.	60	28	12	

50. 6. A method as claimed in claim 1, in which 80-97½ parts by weight of L.D.-slag are treated with 20-2½ parts by weight of schist, calculated as ash.

7. A method as claimed in claim 1, in which blast furnace slag and/or red muds are added to the L.D.-slag.

8. A method as claimed in claim 1, in which the newly formed slag is converted into a portland cement clinker after adding lime.

9. Slag having hydraulic properties, obtained from L.D.-slag treated by a method according to any preceding claim.

10. Portland cement clinker produced from raw materials obtained from L.D.-slag treated by a method according to any preceding claim.

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1556833 COMPLETE SPECIFICATION
1 SHEET *This drawing is a reproduction of
the Original on a reduced scale*

FIG. 1

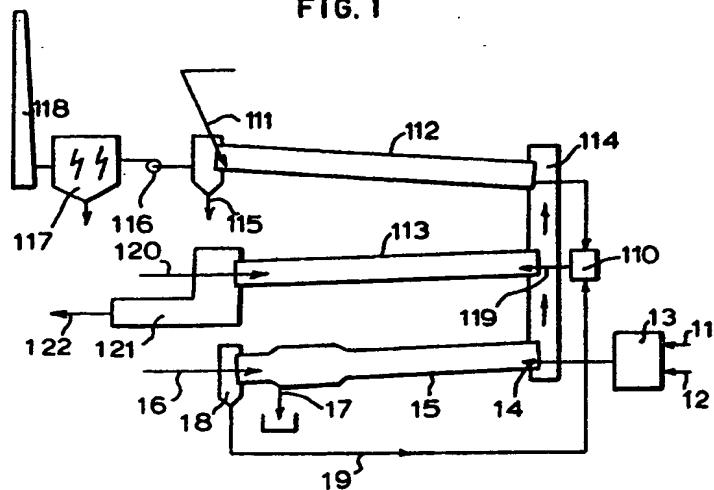


FIG. 2

